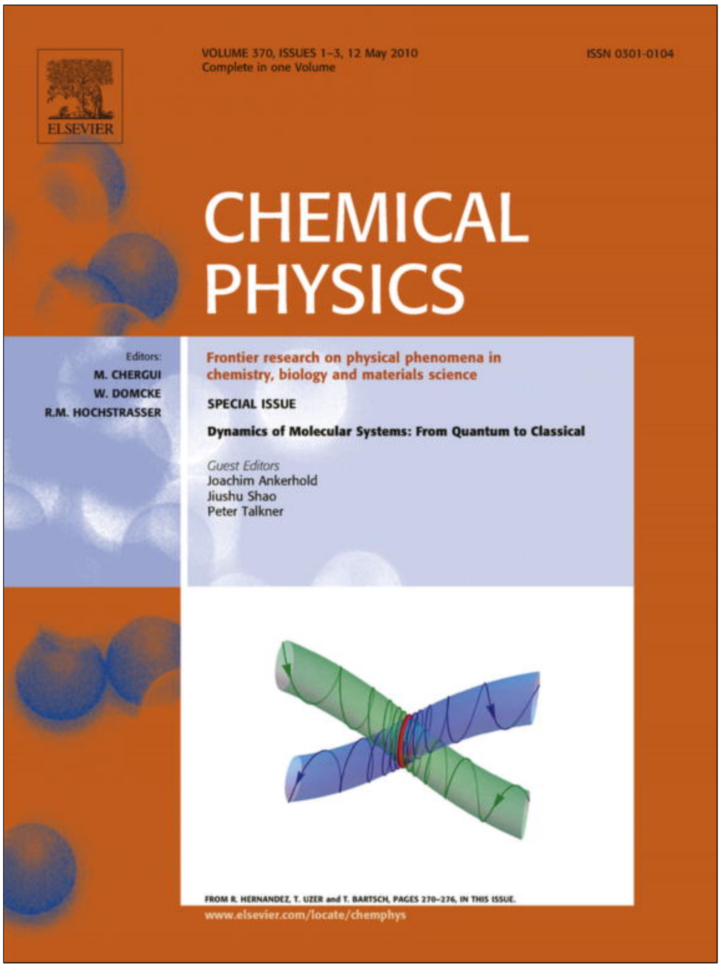
VOLUME 370, ISSUES 1–3, 12 May 2010
Complete in one Volume
ISSN 0301-0104
ELSEVIER
CHEMICAL PHYSICS
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www.elsevier.com/locate/chemphys

Chemical Physics 370 (2010) 253–257

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Variance of residence time spent by diffusing particle in a sub-domain: Path integral based approach

A.M. Berezhkovskii *

Mathematical and Statistical Computing Laboratory, Division of Computational Bioscience, Center for Information Technology, National Institutes of Health, Bethesda, MD 20892, USA

ARTICLE INFO

Article history:
Received 31 August 2009
In final form 23 October 2009
Available online 27 October 2009

Keywords:
Diffusion
Residence time
Fluctuations

ABSTRACT

Path integral based approach is used to analyze the variance of the residence time spent in a sub-domain by a particle diffusing in the presence of an arbitrary potential in a larger domain containing the sub-domain. It is assumed that there is no absorption of the particle within the domain or at its boundaries. Because of the ergodisity, the mean residence time in the sub-domain is a product of the observation time and the equilibrium probability of finding the particle in the sub-domain. We show that the variance also grows linearly with the observation time at large times and explain how the slope of this linear dependence can be found. The general approach is illustrated by simple examples, in which explicit formulas for the variance can be obtained.

Published by Elsevier B.V.

1. Introduction

When developing theory one frequently needs to know how much time a dynamical system spends in a given region of its coordinate/phase space or in a subset of its discrete states. Examples include Taylor dispersion [1,2], single-molecule fluorescence spectroscopy [3–6], channel-facilitated membrane transport [7], chromatography [8], transport in the cytoplasm [9,10] and in tubes with dead ends [11,12], just to mention a few. This residence time, τ_ω, where the subscript ω denotes the subset or the region of interest, is a random variable. When the observation time, t, is long enough and the system dynamics is ergodic, one can easily find the mean residence time, $\langle \tau_\omega(t) \rangle = P_\omega^{eq} t$, $t \to \infty$, where P_ω^{eq} is the equilibrium probability of finding the system in ω.

The focus of the present paper is on the variance of the residence time in a sub-domain ω for a particle that diffuses in a d-dimensional domain Ω in the presence of an arbitrary potential, $U(\mathbf{x})$ (Fig. 1). In the next section we develop a general theory assuming that the distribution of the particle starting point in Ω is the equilibrium one. We show that the variance, $\sigma^2_{\tau_\omega}(t)$, grows linearly with t at large observation times, $\sigma^2_{\tau_\omega}(t) = A_\omega t$, $t \to \infty$, where A_ω is a constant, and explain how this constant can be found. To illustrate the general approach in Section 3 we discuss several simple cases when $U(\mathbf{x}) = 0$ (free diffusion) and Ω is a d-dimensional sphere, $d = 1, 2, 3$, containing a spherical sub-domain ω in its center. In these cases we obtain explicit expressions for the variance that show how it depends on the radii of ω and Ω in spaces of different dimensions. Some concluding remarks are made in Section 4.

The theory developed in the present paper is based on the path integral approach to the problem. An alternative path integral based approach has been used in Ref. [13], which is mainly focused on the distribution of the time spent in a spherical domain by a particle freely diffusing in an unbounded three-dimensional space, assuming that the observation time is infinite. So, the present paper and Ref. [13] complement each other. In Ref. [13] one can also find several useful references that are not mentioned in the present paper. More recent references on studies devoted to the residence time can be found in Ref. [14].

To avoid confusion and to explain what, we believe, is new in the present paper, we indicate that the concept of the residence time has been used in the literature in two different contexts. The concept was used when discussing processes, in which the particle can be trapped or escape to infinity, so that the probability density of its position vanishes as $t \to \infty$. We do not consider such situations here and assume that there is no absorption of the particle within the domain or its boundaries, so that the particle lives forever, and any initial distribution of its position approaches the Boltzmann equilibrium one as $t \to \infty$. Analysis of the relaxation kinetics in such situations was pioneered by Agmon [15], which is focused on the mean relaxation times assuming that the system is spherically symmetric. In this paper we assume that the particle's starting point is taken from the equilibrium Boltzmann distribution. Then the particle is in equilibrium from the very beginning and we need not consider an initial period of relaxation. Our analysis is focused on the variance of the residence time in ω when both the domain and the sub-domain are of arbitrary shape and diffusion occurs in the presence of arbitrary potential, $U(\mathbf{x})$. Main

* Fax: +1 301 496 0825.
E-mail address: berezh@mail.nih.gov

0301-0104/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.chemphys.2009.10.020

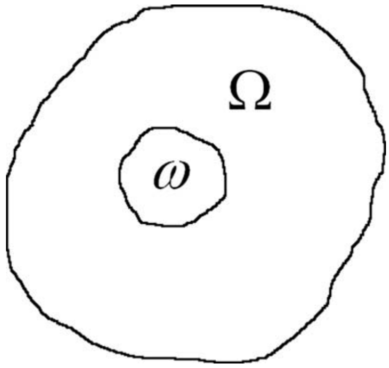

Fig. 1. Schematic representation of domain Ω containing sub-domain ω.

results of this paper are the expressions for the variance given in Eqs. (24) and (37). To our knowledge, they have never been discussed in the literature. However, some intermediate formulas appearing in the course of our analysis can be found, for example, in Refs. [13,15], as well as in the books [16,17].

2. General theory

2.1. Residence time

Consider a particle diffusing in a d-dimensional domain Ω in the presence of an arbitrary potential $U(\mathbf{x})$. There is no absorption of the particle within the domain or at its boundaries, so that any initial distribution of the particle position eventually relaxes to the Boltzmann equilibrium one. We assume that $\int_\Omega \exp[-\beta U(\mathbf{x})]dx$ is finite, where $\beta = 1/(k_BT)$ with the standard notations k_B and T for the Boltzmann constant and the absolute temperature. The domain contains a sub-domain ω as schematically shown in Fig. 1. From time to time the particle enters the sub-domain, spends some time inside, then escapes, then comes back again, and so on. Let $\{\mathbf{x}\}_t$ be a particle trajectory, i.e., a path, along which the particle moves, observed for time t, $\{\mathbf{x}\}_t = \{\mathbf{x}(t'), 0 \le t' \le t\}$, and $I_\omega(\mathbf{x})$ be the indicator function of ω defined as

$$I_\omega(\mathbf{x}) = \int_\omega \delta(\mathbf{x}-\mathbf{x}')d\mathbf{x}' = \begin{cases} 1, & \text{if } \mathbf{x}\in\omega \\ 0, & \text{otherwise} \end{cases} \tag{1}$$

where $\delta(\mathbf{z})$ is the d-dimensional Dirac delta-function. The residence time spent by the trajectory in the sub-domain, $\tau_\omega(\{\mathbf{x}\}_t)$, is given by

$$\tau_\omega(\{\mathbf{x}\}_t) = \int_0^t I_\omega(\mathbf{x}(t'))dt' = \int_\omega d\mathbf{x}\int_0^t \delta(\mathbf{x}(t')-\mathbf{x})dt' \tag{2}$$

This time is a random variable. In what follows we use the definition in Eq. (2) to find the first two moments and then the variance of the residence time assuming the equilibrium Boltzmann initial distribution of the particle starting point in Ω.

2.2. Mean residence time

The mean residence time spent in the sub-domain by a particle that starts from $\mathbf{x}_0$ and is observed for time t, $\langle\tau_\omega(t|\mathbf{x}_0)\rangle$, is the residence time $\tau_\omega(\{\mathbf{x}\}_t)$ averaged over all trajectories that start from $\mathbf{x}_0$. Denoting the averaging over such trajectories by $\langle\cdots\rangle_{\mathbf{x}_0}$ and using Eq. (2) we can write

$$\langle\tau_\omega(t|\mathbf{x}_0)\rangle = \langle\tau_\omega(\{\mathbf{x}\}_t)\rangle_{\mathbf{x}_0} = \int_\omega d\mathbf{x}\int_0^t \langle\delta(\mathbf{x}(t')-\mathbf{x})\rangle_{\mathbf{x}_0}dt' \tag{3}$$

Since the averaged delta-function is the particle propagator,

$$\langle\delta(\mathbf{x}(t)-\mathbf{x})\rangle_{\mathbf{x}_0} = g(\mathbf{x},t|\mathbf{x}_0) \tag{4}$$

we obtain

$$\langle\tau_\omega(t|\mathbf{x}_0)\rangle = \int_\omega d\mathbf{x}\int_0^t g(\mathbf{x},t'|\mathbf{x}_0)dt' \tag{5}$$

Introducing the notation $P_\omega(t|\mathbf{x}_0)$ for the probability of finding the particle in the sub-domain at time t,

$$P_\omega(t|\mathbf{x}_0) = \int_\omega g(\mathbf{x},t|\mathbf{x}_0)d\mathbf{x} \tag{6}$$

we can write $\langle\tau_\omega(t|\mathbf{x}_0)\rangle$ as

$$\langle\tau_\omega(t|\mathbf{x}_0)\rangle = \int_0^t P_\omega(t'|\mathbf{x}_0)dt' \tag{7}$$

As $t\to\infty$, $P_\omega(t|\mathbf{x}_0)$ approaches its equilibrium value P_ω^{eq},

$$P_\omega^{eq} = \int_\omega p_{eq}(\mathbf{x})d\mathbf{x} \tag{8}$$

where $p_{eq}(\mathbf{x}) = Z^{-1}\exp[-\beta U(\mathbf{x})]$ is the equilibrium distribution in Ω with $Z = \int_\Omega \exp[-\beta U(\mathbf{x})]d\mathbf{x}$. As a result, at large times $\langle\tau_\omega(t|\mathbf{x}_0)\rangle$ takes the asymptotic form, $P_\omega^{eq}t$. This is a consequence of the ergodicity of the diffusive motion.

Averaging $\langle\tau_\omega(t|\mathbf{x}_0)\rangle$ in Eq. (5) over the equilibrium distribution of the particle starting point in Ω and denoting the result by $\langle\langle\tau_\omega(t)\rangle\rangle_{eq}$ we obtain

$$\begin{aligned}\langle\langle\tau_\omega(t)\rangle\rangle_{eq} &= \int_\Omega \langle\tau_\omega(t|\mathbf{x}_0)\rangle p_{eq}(\mathbf{x}_0)d\mathbf{x}_0 \\ &= \int_0^t dt'\int_\omega d\mathbf{x}\int_\Omega g(\mathbf{x},t'|\mathbf{x}_0)p_{eq}(\mathbf{x}_0)d\mathbf{x}_0\end{aligned} \tag{9}$$

The integral over Ω is equal to $p_{eq}(\mathbf{x})$ independently of time,

$$\int_\Omega g(\mathbf{x},t|\mathbf{x}_0)p_{eq}(\mathbf{x}_0)d\mathbf{x}_0 = p_{eq}(\mathbf{x}) \tag{10}$$

Using this fact and the definition of P_ω^{eq}, Eq. (8), we arrive at

$$\langle\langle\tau_\omega(t)\rangle\rangle_{eq} = P_\omega^{eq}t \tag{11}$$

Thus, for the equilibrium distribution of the particle starting point in Ω this relation is true not only at asymptotically large times, but at any moment of time, $t \geqslant 0$.

2.3. Variance of the residence time

The second moment of the particle residence time in the sub-domain, Eq. (2), on condition that the particle starts from $\mathbf{x}_0$, $\langle\tau_\omega^2(t|\mathbf{x}_0)\rangle$, is given by

$$\begin{aligned}\langle\tau_\omega^2(t|\mathbf{x}_0)\rangle &= \langle[\tau_\omega(\{\mathbf{x}\}_t)]^2\rangle_{\mathbf{x}_0} \\ &= \left\langle\left[\int_0^t I_\omega(\mathbf{x}(t_1))dt_1\right]\left[\int_0^t I_\omega(\mathbf{x}(t_2))dt_2\right]\right\rangle_{\mathbf{x}_0}\end{aligned} \tag{12}$$

Interchanging the averaging over trajectories and the integrations with respect to time we obtain

$$\langle\tau_\omega^2(t|\mathbf{x}_0)\rangle = 2\int_0^t dt_2\int_0^{t_2}\langle I_\omega(\mathbf{x}(t_2))I_\omega(\mathbf{x}(t_1))\rangle_{\mathbf{x}_0}dt_1 \tag{13}$$

where we have used the symmetry of function $\langle I_\omega(\mathbf{x}(t_1))I_\omega(\mathbf{x}(t_2))\rangle_{\mathbf{x}_0}$. This function can be expressed in terms of the particle propagator. To show this, consider the function at $t_2 > t_1$. Using the definition of the indicator function, Eq. (1), we can write

$$\langle I_\omega(\mathbf{x}(t_1))I_\omega(\mathbf{x}(t_2))\rangle_{\mathbf{x}_0} = \int_\omega\int_\omega \langle\delta(\mathbf{x}(t_2)-\mathbf{x}_2)\delta(\mathbf{x}(t_1)-\mathbf{x}_1)\rangle_{\mathbf{x}_0}d\mathbf{x}_1\,d\mathbf{x}_2 \tag{14}$$

For $t_2 > t_1$ we have

$$\langle\delta(\mathbf{x}(t_2)-\mathbf{x}_2)\delta(\mathbf{x}(t_1)-\mathbf{x}_1)\rangle_{\mathbf{x}_0} = g(\mathbf{x}_2,t_2-t_1|\mathbf{x}_1)g(\mathbf{x}_1,t_1|\mathbf{x}_0) \tag{15}$$

where the definition of the propagator, Eq. (4), has been used. Combining the relations in Eqs. (13)–(15) we arrive at

$$\langle \tau_\omega^2(t|\mathbf{x}_0)\rangle = 2\int_0^t dt_2 \int_0^{t_2} dt_1 \int_\omega \int_\omega g(\mathbf{x}_2, t_2 - t_1|\mathbf{x}_1) g(\mathbf{x}_1, t_1|\mathbf{x}_0) d\mathbf{x}_1\, d\mathbf{x}_2 \tag{16}$$

We denote the equilibrium average of $\langle \tau_\omega^2(t|\mathbf{x}_0)\rangle$ over the particle starting points by $\langle\langle \tau_\omega^2(t)\rangle\rangle_{eq}$,

$$\langle\langle \tau_\omega^2(t)\rangle\rangle_{eq} = \int_\Omega \langle \tau_\omega^2(t|\mathbf{x}_0)\rangle p_{eq}(\mathbf{x}_0) d\mathbf{x}_0 \tag{17}$$

Using Eq. (16) and the relation in Eq. (10) we obtain

$$\langle\langle \tau_\omega^2(t)\rangle\rangle_{eq} = 2\int_0^t dt_2 \int_0^{t_2} dt_1 \int_\omega \int_\omega g(\mathbf{x}_2, t_2 - t_1|\mathbf{x}_1) p_{eq}(\mathbf{x}_1) d\mathbf{x}_1\, d\mathbf{x}_2 \tag{18}$$

The propagator approaches the equilibrium distribution as $t \to \infty$. With this in mind we can write the propagator as

$$g(\mathbf{x}, t|\mathbf{x}_0) = p_{eq}(\mathbf{x}) + u(\mathbf{x}, t|\mathbf{x}_0) \tag{19}$$

Substituting this into Eq. (18) and carrying out the integrations of $p_{eq}(\mathbf{x})$ over ω we arrive at

$$\langle\langle \tau_\omega^2(t)\rangle\rangle_{eq} = (P_\omega^{eq} t)^2 + 2\int_0^t dt_2 \int_0^{t_2} dt_1 \int_\omega \int_\omega u(\mathbf{x}_2, t_2 - t_1|\mathbf{x}_1) p_{eq}(\mathbf{x}_1) d\mathbf{x}_1\, d\mathbf{x}_2 \tag{20}$$

where we have used the definition of P_ω^{eq}, Eq. (8).

Since $P_\omega^{eq} t = \langle\langle \tau_\omega(t)\rangle\rangle_{eq}$ we can find the variance of the particle residence time in the sub-domain, $\sigma_{\tau_\omega}^2(t)$,

$$\begin{aligned}\sigma_{\tau_\omega}^2(t) &= \langle\langle \tau_\omega^2(t)\rangle\rangle_{eq} - \langle\langle \tau_\omega(t)\rangle\rangle_{eq}^2 \\ &= 2\int_0^t dt_2 \int_0^{t_2} dt_1 \int_\omega \int_\omega u(\mathbf{x}_2, t_2 - t_1|\mathbf{x}_1) p_{eq}(\mathbf{x}_1) d\mathbf{x}_1\, d\mathbf{x}_2\end{aligned} \tag{21}$$

By construction, $u(\mathbf{x},t|\mathbf{x}_0)$ vanishes as $t \to \infty$, and its integral with respect to time from zero to infinity is finite. We use this to find the long-time asymptotic behavior of the variance,

$$\sigma_{\tau_\omega}^2(t) = 2t \int_\omega \int_\omega \left[\int_0^\infty u(\mathbf{x}, t'|\mathbf{x}_0) dt'\right] p_{eq}(\mathbf{x}_0) d\mathbf{x}\, d\mathbf{x}_0, \quad t \to \infty \tag{22}$$

Introducing function $w_\omega(\mathbf{x})$ defined by

$$w_\omega(\mathbf{x}) = \int_\omega \left[\int_0^\infty u(\mathbf{x}, t|\mathbf{x}_0) dt\right] p_{eq}(\mathbf{x}_0) d\mathbf{x}_0 \tag{23}$$

we can write the variance, Eq. (22), as

$$\sigma_{\tau_\omega}^2(t) = 2t \int_\omega w_\omega(\mathbf{x}) d\mathbf{x}, \quad t \to \infty \tag{24}$$

Thus, to find the asymptotic behavior of the variance, one has to find the function $w_\omega(\mathbf{x})$ and then to integrate it over the sub-domain.

Function $w_\omega(\mathbf{x})$ satisfies the equation that can be derived starting with the evolution equation for the propagator,

$$\frac{\partial g(\mathbf{x}, t|\mathbf{x}_0)}{\partial t} = \widehat{L} g(\mathbf{x}, t|\mathbf{x}_0) \tag{25}$$

where $\widehat{L}$ is the Smoluchowski evolution operator,

$$\widehat{L} = D\nabla\left\{p_{eq}(\mathbf{x})\nabla\left[\frac{1}{p_{eq}(\mathbf{x})}\right]\right\} \tag{26}$$

and D is the particle diffusion coefficient. Integrating both sides of Eq. (25) with respect to time from zero to infinity and using Eq. (19) we obtain

$$p_{eq}(\mathbf{x}) - \delta(\mathbf{x} - \mathbf{x}_0) = \widehat{L} \int_0^\infty u(\mathbf{x}, t|\mathbf{x}_0) dt \tag{27}$$

Multiplying both sides of this equation by $p_{eq}(\mathbf{x}_0)$ and integrating with respect to $\mathbf{x}_0$ over the sub-domain, we arrive at the desirable equation for the function $w_\omega(\mathbf{x})$

$$\widehat{L} w_\omega(\mathbf{x}) = [P_\omega^{eq} - I_\omega(\mathbf{x})] p_{eq}(\mathbf{x}) \tag{28}$$

Note that function $w_\omega(\mathbf{x})$ found by integrating this equation satisfies the relation

$$\int_\Omega w_\omega(\mathbf{x}) d\mathbf{x} = 0 \tag{29}$$

This is a consequence of the fact that function $u(\mathbf{x}, t|\mathbf{x}_0)$ is the difference of the propagator and the equilibrium distribution and, therefore, satisfies

$$\int_\Omega u(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x} = \int_\Omega [g(\mathbf{x}, t|\mathbf{x}_0) - p_{eq}(\mathbf{x})] d\mathbf{x} = 0 \tag{30}$$

The relation in Eq. (29) follows from this and the definition of function $w_\omega(\mathbf{x})$, Eq. (23).

To summarize, one can find function $w_\omega(\mathbf{x})$ by integrating Eq. (28) and then use this function to find the variance by means of Eq. (24). This is one of the major results of the present paper. To illustrate the approach, in the next section we find the variance in several cases of simple geometry where explicit expressions for the variance can be obtained.

Finally we point out that the variance, Eqs. (22) and (24), has an interesting interpretation. To show this we introduce function $v_\omega(\mathbf{x}_0)$ defined by

$$v_\omega(\mathbf{x}_0) = \int_\omega \left[\int_0^\infty u(\mathbf{x}, t|\mathbf{x}_0) dt\right] d\mathbf{x} \tag{31}$$

Using this function the variance, Eq. (22), can be written as

$$\sigma_{\tau_\omega}^2(t) = 2t \int_\omega v_\omega(\mathbf{x}_0) p_{eq}(\mathbf{x}_0) d\mathbf{x}_0, \quad t \to \infty \tag{32}$$

Interchanging the order of integrations and using Eqs. (6), (8), and (19) we can write function $v_\omega(\mathbf{x}_0)$, Eq. (31), in the form

$$v_\omega(\mathbf{x}_0) = \int_0^\infty [P_\omega(t|\mathbf{x}_0) - P_\omega^{eq}] dt \tag{33}$$

Next we introduce the relaxation function, $R_\omega(t|\mathbf{x}_0)$,

$$R_\omega(t|\mathbf{x}_0) = \frac{P_\omega(t|\mathbf{x}_0) - P_\omega^{eq}}{P_\omega(0|\mathbf{x}_0) - P_\omega^{eq}} = \frac{P_\omega(t|\mathbf{x}_0) - P_\omega^{eq}}{I_\omega(\mathbf{x}_0) - P_\omega^{eq}} \tag{34}$$

and the relaxation time, $\langle t_\omega^{rel}(\mathbf{x}_0)\rangle$, defined as the time integral of the relaxation function,

$$\langle t_\omega^{rel}(\mathbf{x}_0)\rangle = \int_0^\infty R_\omega(t|\mathbf{x}_0) dt \tag{35}$$

This allows us to write function $v_\omega(\mathbf{x}_0)$, Eq. (33), as

$$v_\omega(\mathbf{x}_0) = [I_\omega(\mathbf{x}_0) - P_\omega^{eq}]\langle t_\omega^{rel}(\mathbf{x}_0)\rangle \tag{36}$$

Substituting this into Eq. (32) we obtain

$$\sigma_{\tau_\omega}^2(t) = 2t\langle\langle t_\omega^{rel}\rangle\rangle_{eq} P_\omega^{eq}(1 - P_\omega^{eq}), \quad t \to \infty \tag{37}$$

where $\langle\langle t_\omega^{rel}\rangle\rangle_{eq}$ is the relaxation time $\langle t_\omega^{rel}(\mathbf{x}_0)\rangle$ averaged over the equilibrium distribution of the starting points in the sub-domain,

$$\langle\langle t_\omega^{rel}\rangle\rangle_{eq} = \frac{1}{P_\omega^{eq}} \int_\omega \langle t_\omega^{rel}(\mathbf{x}_0)\rangle p_{eq}(\mathbf{x}_0) d\mathbf{x}_0 \tag{38}$$

Comparison of the two expressions for the variance, Eqs. (24) and (37), shows that the averaged relaxation time can be written as

$$\langle\langle t_{\omega}^{rel}\rangle\rangle_{eq} = \frac{1}{P_{\omega}^{eq}(1-P_{\omega}^{eq})}\int_{\omega} w_{\omega}(\mathbf{x})d\mathbf{x} \tag{39}$$

Note that the relaxation time remains finite when P_{ω}^{eq} approaches zero or unity since the integral over ω vanishes in both cases, i.e., when ω tends to zero or Ω. The expression for the variance in Eq. (37) shows that the variance is proportional to the equilibrium average of the relaxation time. This expression also shows that the variance vanishes when P_{ω}^{eq} tends to zero and unity, i.e., when the sub-domain collapses into a point or approaches the entire domain.

3. Illustrative examples

3.1. Diffusion on an interval

Consider a particle freely diffusing in one dimension on an interval of length L, $0 < x < L$, terminated by reflecting end points at $x = 0$ and $x = L$ (domain Ω). The quantity of our interest is the variance of the time spent by the particle inside the shorter interval of length l, $0 < x < l$, $l \leqslant L$ (sub-domain ω). The long-time asymptotic behavior of this variance is given by Eq. (24), which in the case under consideration takes the form

$$\sigma_{\tau_\omega}^2(t) = 2t\int_0^l w_{\omega}(x)dx, \quad t\to\infty \tag{40}$$

Function $w_{\omega}(x)$ satisfies Eq. (28) that can be written as

$$D\frac{d^2w_{\omega}(x)}{dx^2} = \frac{1}{L}\left[\frac{l}{L} - H(l-x)\right], \quad 0<x<L \tag{41}$$

where $H(z)$ is the Heaviside step function and we have used the fact that in the present case $p_{eq}(x) = 1/L$, $P_{\omega}^{eq} = l/L$, and the indicator function, Eq. (1), is given by $I_{\omega}(x) = H(l - x)$. Function $w_{\omega}(x)$ satisfies reflecting boundary condition at $x = 0$, $dw_{\omega}(x)/dx|_{x=0} = 0$ and the relation

$$\int_0^L w_{\omega}(x)dx = 0 \tag{42}$$

which follows from Eq. (29).

Integrating Eq. (41) we obtain

$$w_{\omega}(x) = \frac{1}{6L^2D}\times\begin{cases}(L-l)[l(2L-l)-3x^2], & 0<x<l\\ l[2L^2+l^2-6Lx+3x^2], & l<x<L\end{cases} \tag{43}$$

Substituting this into Eq. (40) and carrying out the integration we arrive at

$$\sigma_{\tau_\omega}^2(t) = \frac{2l^2(L-l)^2t}{3L^2D}, \quad t\to\infty \tag{44}$$

Next we use Eq. (39) to find the averaged relaxation time. In the case under consideration this equation takes the form

$$\langle\langle t_{\omega}^{rel}\rangle\rangle_{eq} = \frac{1}{P_{\omega}^{eq}(1-P_{\omega}^{eq})}\int_0^l w_{\omega}(x)dx \tag{45}$$

and leads to

$$\langle\langle t_{\omega}^{rel}\rangle\rangle_{eq} = \frac{l(L-l)}{3D} \tag{46}$$

The formulas in Eqs. (44) and (46) show that both the variance and the averaged relaxation time vanish as l approaches zero or L.

3.2. Diffusion inside a circle

Consider a particle freely diffusing inside a circle of radius R (domain Ω). This time we are interested in the variance of the time spent by the particle inside the smaller circle of radius a, $a \leqslant R$, (sub-domain ω) concentric with the initial larger circle. In the case under consideration $p_{eq}(\mathbf{r}) = 1/(\pi R^2)$, $P_{\omega}^{eq} = a^2/R^2$, and the indicator function, Eq. (1), has the form $I_{\omega}(\mathbf{r}) = H(a - r)$. The asymptotic behavior of the variance, Eq. (24), in this case is given by

$$\sigma_{\tau_\omega}^2(t) = 4\pi t\int_0^a w_{\omega}(r)r\,dr, \quad t\to\infty \tag{47}$$

Function $w_{\omega}(r)$ satisfies Eq. (28) that can be written as

$$\frac{D}{r}\frac{d}{dr}\left[r\frac{dw_{\omega}(r)}{dr}\right] = \frac{1}{\pi R^2}\left[\frac{a^2}{R^2} - H(a-r)\right], \quad 0<r<R \tag{48}$$

When integrating this equation we use the reflecting boundary condition at the origin, $dw_{\omega}(r)/dr|_{r=0} = 0$ and the relation

$$\int_0^R w_{\omega}(r)r\,dr = 0 \tag{49}$$

that follows from Eq. (29).

Integrating Eq. (48) we obtain

$$w_{\omega}(r) = \begin{cases} w_{\omega}(0) - \frac{R^2-a^2}{4\pi R^4D}r^2, & 0<r<a\\ w_{\omega}(0) - \frac{a^2}{4\pi R^2D}\left[1+2\ln\left(\frac{r}{a}\right) - \frac{r^2}{R^2}\right], & a<r<R\end{cases} \tag{50}$$

where $w_{\omega}(0)$ is given by

$$w_{\omega}(0) = \frac{a^2}{8\pi R^2D}\left[4\ln\left(\frac{R}{a}\right) - 1 + \frac{a^2}{R^2}\right] \tag{51}$$

Substituting $w_{\omega}(r)$, Eq. (50), into Eq. (47) and carrying out the integration we arrive at

$$\sigma_{\tau_\omega}^2(t) = \left[2\ln\left(\frac{R}{a}\right) - 1 + \frac{a^2}{R^2}\right]\frac{a^4t}{2R^2D}, \quad t\to\infty \tag{52}$$

The averaged relaxation time in Eq. (39) in the case under consideration takes the form

$$\langle\langle t_{\omega}^{rel}\rangle\rangle_{eq} = \frac{2\pi}{P_{\omega}^{eq}(1-P_{\omega}^{eq})}\int_0^a w_{\omega}(r)r\,dr \tag{53}$$

Its explicit dependence on the two radii is

$$\langle\langle t_{l}^{rel}\rangle\rangle_{eq} = \left[2\ln\left(\frac{R}{a}\right) - 1 + \frac{a^2}{R^2}\right]\frac{a^2R^2}{4(R^2-a^2)D} \tag{54}$$

The formulas in Eqs. (52) and (54) show that both the variance and the averaged relaxation time vanish as a approaches zero or R.

3.3. Diffusion inside a sphere

Finally we consider a particle freely diffusing in three dimensions inside a sphere of radius R (domain Ω). We wish to find the long-time asymptotic behavior of the variance of the time spent by the particle inside the concentric sphere of smaller radius a, $a \leqslant R$ (sub-domain ω). In the case under consideration $p_{eq}(\mathbf{r}) = 3/(4\pi R^3)$, $P_{\omega}^{eq} = a^3/R^3$, and the indicator function, Eq. (1), has the form $I_{\omega}(\mathbf{r}) = H(a - r)$. The asymptotic behavior of the variance, Eq. (24), in this case is given by

$$\sigma_{\tau_\omega}^2(t) = 8\pi t\int_0^a w_{\omega}(r)r^2\,dr, \quad t\to\infty \tag{55}$$

Function $w_{\omega}(r)$ satisfies Eq. (28) that can be written as

$$\frac{D}{r^2}\frac{d}{dr}\left[r^2\frac{dw_{\omega}(r)}{dr}\right] = \frac{3}{4\pi R^3}\left[\frac{a^3}{R^3} - H(a-r)\right], \quad 0<r<R \tag{56}$$

When integrating this equation we use the reflecting boundary condition at the origin, $dw_{\omega}(r)/dr|_{r=0} = 0$ and the relation

$$\int_0^R w_\omega(r) r^2\, dr = 0 \tag{57}$$

that follows from Eq. (29).

Integrating Eq. (56) we obtain

$$w_\omega(r) = \begin{cases} w_\omega(0) - \frac{R^3 - a^3}{8\pi R^6 D} r^2, & 0 < r < a \\ w_\omega(0) - \frac{3a^2}{8\pi R^3 D}\left(1 - \frac{2a}{3r} - \frac{ar^2}{3R^3}\right), & a < r < R \end{cases} \tag{58}$$

where $w_\omega(0)$ is given by

$$w_\omega(0) = \frac{3a^2}{8\pi R^3 D}\left(1 - \frac{6a}{5R} + \frac{a^3}{5R^3}\right) \tag{59}$$

Substituting $w_\omega(r)$, Eq. (58), into Eq. (55) and carrying out the integration we arrive at

$$\sigma^2_{\tau_\omega}(t) = \left(1 - \frac{3a}{2R} + \frac{a^3}{2R^3}\right)\frac{4a^5 t}{5R^3 D}, \quad t \to \infty \tag{60}$$

The averaged relaxation time in Eq. (39) in the case under consideration takes the form

$$\langle\langle t^{rel}_\omega \rangle\rangle_{eq} = \frac{4\pi}{P^{eq}_\omega (1 - P^{eq}_\omega)} \int_0^a w_\omega(r) r^2\, dr \tag{61}$$

Its explicit dependence on the two radii is

$$\langle\langle t^{rel}_l \rangle\rangle_{eq} = \left(1 - \frac{3a}{2R} + \frac{a^3}{2R^3}\right)\frac{2a^2 R^3}{5(R^3 - a^3)D} \tag{62}$$

The formulas in Eqs. (60) and (62) show that both the variance and the averaged relaxation time vanish as a approaches zero or R.

4. Concluding remarks

The present paper deals with a particle that diffuses in a d-dimensional domain Ω in the presence of an arbitrary potential $U(\mathbf{x})$ and occasionally visits a sub-domain ω (Fig. 1). The residence time in the sub-domain, τ_ω, is a random variable. One can easily find the mean residence time using the fact that diffusive dynamics is ergodic. In the present paper we discuss the variance of the residence time, $\sigma^2_{\tau_\omega}(t)$, assuming equilibrium distribution of the particle starting point over the entire domain Ω. We show that the variance linearly grows with time at large times, $\sigma^2_{\tau_\omega}(t) = A_\omega t$, $t \to \infty$, with $A_\omega = 2\int_\omega w_\omega(\mathbf{x}) d\mathbf{x}$, where function $w_\omega(\mathbf{x})$ can be found by integrating Eq. (28). We also establish the relation between A_ω and the relaxation time defined in Eq. (38), $A_\omega = 2P^{eq}_\omega(1 - P^{eq}_\omega)\langle\langle t^{rel}_\omega\rangle\rangle_{eq}$. Our general approach is illustrated by applying the formalism to the cases of simple geometries, where explicit formulas for the variance can be obtained.

Our analysis is based on the path integral approach to the problem. We start with the definitions of the quantities of interest in terms of the path integral. Then we use the relations in Eqs. (4) and (15) that allow us to express these quantities in terms of the propagator. Next we split the propagator into its long-time asymptotic part, $p_{eq}(\mathbf{x})$, and the "relaxation" part, $u(\mathbf{x}, t|\mathbf{x}_0)$, that vanishes at large times, Eq. (19). This representation of the propagator is used when deriving Eq. (28). We hope that our results will be of use in the future studies.

Acknowledgements

The author is greatly obliged to his colleagues at NIH, Sergey Bezrukov, Irina Gopich, Attila Szabo, and George Weiss, as well as his colleagues in Israel, Mexico and Russia, Noam Agmon, Leonardo Dagdug, Yurii Makhnovskii, and Vladimir Zitserman, for very useful and illuminating discussions of different aspects of the residence time distribution and related problems. This study was supported by the Intramural Research Program of the NIH, Center for Information Technology.

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